Catalytic properties of ultrafine molybdenum–cerium oxide particles prepared by the sol–gel method

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The structure and catalytic properties of ultrafine Mo–Ce oxide particles prepared by the sol–gel method have been studied by using X-ray diffraction, transmission electron microscopy, temperature-programmed reduction, laser Raman spectroscopy and microreactor tests. It has been shown that for selective oxidation of toluene to benzaldehyde the ultrafine Mo–Ce oxide particles exhibit higher catalytic activity than the larger oxide particles prepared by a conventional coprecipitation method. The unique catalytic properties of ultrafine Mo–Ce oxide particles may be correlated not only to the interaction between molybdenum oxide and cerium oxide, but also to the higher reactivity of lattice oxygen species in the ultrafine oxide matrix.

Keywords: ultrafine particles, Mo–Ce oxides, selective oxidation

1. Introduction

C–H activation leading to selective oxidation is one of the most challenging problems in terms of surface science and catalysis. In the past decades, many kinds of metal oxides, especially Mo-based and V-based oxides, have been widely used as selective oxidation catalysts, and the studies on the structure and catalytic properties of these oxides have demonstrated that the nature of oxygen species is one of the most important parameters influencing catalytic selectivity. For the oxidation of olefins and aromatics on oxide catalysts, the nucleophilic lattice oxygen ions (O^{2-}) are responsible for the selective oxidation; while electrophilic oxygen species (O_2^-, O^-) may attack C=C bonds and benzene rings because of higher electron density in these regions, which leads to C–C bond cleavage and complete oxidation [1,2]. In order to increase the reactivity of lattice oxygen species and to improve the catalytic selectivity, great efforts have been made to modify the state of lattice oxygen species by adding some promoters to these oxides [3]. It has been found that Bi, Fe, Sn, W and rare earth oxides are effective promoters of the molybdenum-based and vanadium-based oxide catalysts for selective oxidation of toluene to benzaldehyde [4–9].

In the latest years, ultrafine metal oxides have attracted much research interest in terms of materials science and heterogeneous catalysis [10,11]. These new catalytic materials are expected to have unique catalytic properties because of their nanoscale particle sizes. Among the different methods for preparation of ultrafine oxide particles, the sol–gel technique has received widespread attention because of its potential in delivering samples that are better mixed on a molecular scale, which provides an opportunity for tailoring the chemical and structural properties of oxide catalysts [12,13]. In this work, a novel catalyst for selective oxidation of toluene to benzaldehyde, i.e., ultrafine complex molybdenum cerium oxide particles, has been developed. It has been found that the reactivity of lattice oxygen ions can be improved by decreasing the oxide particle size to nanoscale and that the ultrafine oxide particles exhibit unique catalytic properties for selective oxidation. Our results have revealed that the ultrafine complex oxide particles are potentially new catalytic materials for selective oxidation reactions.

2. Experimental

2.1. Catalyst preparation

In the conventional sol–gel process, alkoxides were often used as starting materials for preparation of metal oxides. In our cases, ultrafine Mo–Ce oxide particle catalysts with different Ce / Mo atomic ratios were prepared by a modified sol–gel method as reported in the literature [14,15], in which inorganic salts were used. Nitrate cerium $Ce(NO_3)_3 \cdot 6H_2O$, ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$ and citric acid aqueous solutions were prepared separately and then mixed with the molar ratio of citric acid to metallic ions of 1 : 3. The pH of the mixture solutions was adjusted to 0.5 with the addition of nitric acid solution. Due to the strong complex effect of citric acid on cerium ions and the low pH of the solution, the above solutions showed high homogeneity without any precipitates. The above solutions were first kept in a water bath at 80°C until gelation was completed, and then the as-prepared gels were dried at 120°C for 4 h and calcined in air at 400°C for 4 h. The mono-component CeO_2 and MoO_3 oxides were prepared by the same procedures. For comparison, the conventional coprecipitation method was also used to prepare Mo–Ce (cp) oxide, in which nitrate cerium aqueous solution was mixed with ammonium molybdate aqueous solution, and the precipitates formed were dried and calcined.

2.2. Catalytic oxidation of toluene

The toluene oxidation reaction was used as a probe to study the catalytic properties of the Mo–Ce complex oxides. The oxides (250 mg) were introduced into a U-type quartz fixed-bed microreactor, and their catalytic properties for selective oxidation of toluene to benzaldehyde were evaluated under the reaction conditions of 0.1 MPa, 400°C, air/toluene $= 9$ (vol/vol), $F/W = 1900$ ml/(h g-cat.) The reaction products were analyzed by an on-line gas chromatograph. Under the above reaction conditions, the main products were mainly CO, CO_2, H_2O and benzaldehyde.

The catalytic properties of ultrafine Mo–Ce oxide catalyst without gaseous oxygen were also determined in a pulse microreactor under the conditions of 350°C, 0.2 MPa, helium flow rate of 40 ml/min, and 0.81 mmol toluene every pulse. For the reaction, samples were pretreated in a helium flow at 400°C for the removal of adsorbed oxygen species. The reaction products, were found to be chiefly benzaldehyde and H_2O.

2.3. Characterization

X-ray diffraction patterns were obtained in a Shimadzu-3A diffractometer with Cu Kα radiation (0.15418 nm). The particles' shape and size were elucidated by TEM with a JEM-100S transmission electron microscopy. BET surface area measurements were performed on a micromeritics ASAP-2000 instrument (N_2 adsorption at 77 K). TPR experiments were carried out in a U-type quartz reactor with a heating rate of 10°C/min, and a flow rate of H_2–Ar mixture (5.0 vol% hydrogen) of ca. 30 ml/min. Hydrogen consumption was monitored by a thermal conductivity detector. The Raman spectra were measured with a BIO-RAD FTS-65A laser Raman spectrometer.

3. Results and discussion

The morphology of a Mo–Ce oxide sample (Ce/Mo atomic ratio $= 2/3$) prepared by sol–gel methods is presented in figure 1. It can be seen that the size of the Mo–Ce oxide particles is in the range of 20–40 nm. This suggests that the Mo–Ce oxide prepared by the sol–gel method is actually ultrafine oxide particles (< 100 nm). The BET surface area of the sample is 20.3 m^2/g. XRD results reveal that molybdenum oxide and cerium oxide species in the Mo–Ce complex oxide sample form a solid solution with a sheelite-type structure of $Ce_2(MoO_4)_3$. On increasing the Ce/Mo atomic ratio to higher than 2/3, however, $Ce_2(MoO_4)_3$ and CeO_2 are found to coexist in the complex oxide samples; while for samples with a Ce/Mo atomic ratio of less than 2/3, $Ce_2(MoO_4)_3$ and MoO_3 are found.

Oxidation of toluene is employed to evaluate the catalytic activity and selectivity of complex Mo–Ce oxides. It is found that the particle size, surface area and structure of ultrafine complex Mo–Ce oxide particles are not changed after reaction. This suggests that the ultrafine oxide particles are quite stable during the catalytic oxidation. After reaction for 7 h, the catalytic oxidation reaches a steady state. The specific activities (benzaldehyde yield per second per BET surface area of catalysts) of Mo–Ce catalysts with different Ce/Mo atomic ratios are shown in figure 2. It can be seen that the maximum catalytic activities for selective oxidation of toluene to benzaldehyde are reached in the vicinity of Ce/

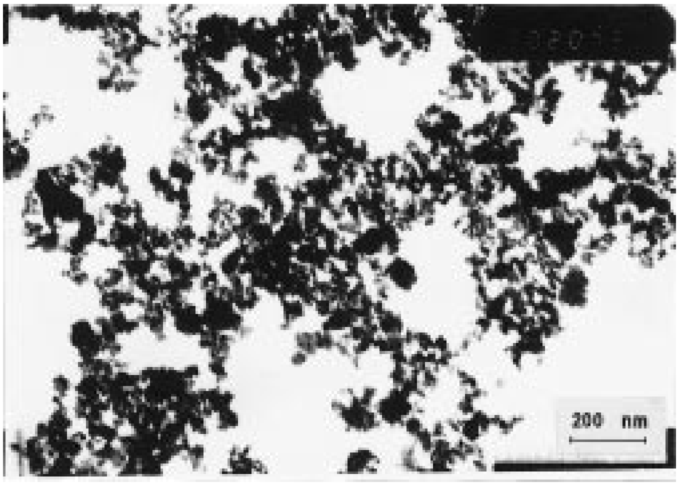

Figure 1. Morphology of $Ce_2(MoO_4)_3$ particles prepared by the sol–gel method.

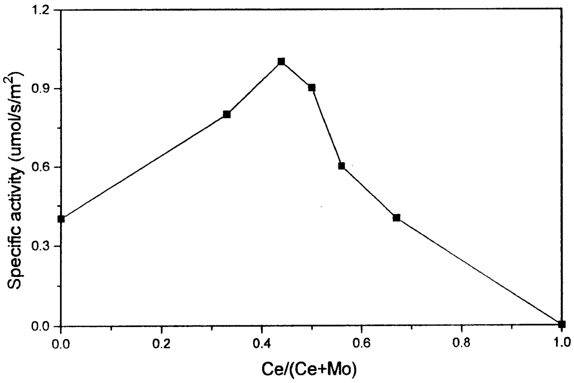

Figure 2. The specific activities of Mo–Ce oxide catalysts with different Ce/Mo atomic ratios.

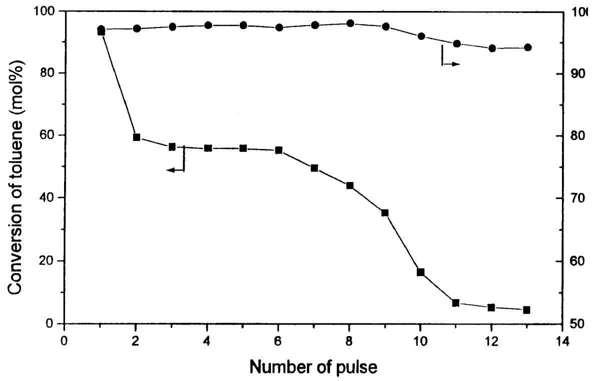

Figure 3. The catalytic properties of Mo–Ce (sg) oxide catalyst with a Ce/Mo atomic ratio of 1.0 for selective oxidation of toluene to benzaldehyde in a pulse microreactor without gaseous oxygen in the feed.

Mo = 1.0 for Mo–Ce catalysts, suggesting that the compositions of complex oxides have great influences on the catalytic properties of the ultrafine oxide particle catalysts.

The catalytic properties of CeO_2, MoO_3, the ultrafine Mo–Ce oxide particles with a Ce/Mo atomic ratio of 1.0 and the corresponding larger oxide particles having the same composition prepared by conventional precipitation method are listed in table 1. It can be seen that under the same reaction conditions, the toluene conversions on the above oxide catalysts show decreasing activity orders of CeO_2 > Mo–Ce (cp)≈Mo–Ce (sg) > MoO_3. The oxidation products on a mono-component CeO_2 catalyst are CO, CO_2 and H_2O, but without benzaldehyde or other selective oxidation products, indicating that CeO_2 is an active component for complete oxidation of toluene. By adding ceria to MoO_3, however, the selectivity to benzaldehyde is improved remarkably, so that the complex oxides show higher specific activity than the mono-component MoO_3 catalyst. Interestingly, the conversions of toluene on both complex Mo–Ce oxides are very similar, but the benzaldehyde selectivity of the ultrafine particle catalyst is much higher than that of the larger particles. These results reveal that ultrafine oxide particle catalysts have unique catalytic properties for the selective oxidation of toluene to benzaldehyde. In particular, the specific activity of the ultrafine oxide particle catalyst is higher than those of the larger oxide particle and the mono-component MoO_3 catalysts, which cannot be explained by the effect of mere particle size. Apparently, the differences in the nature of active oxygen species in the oxide catalysts for selective oxidation of toluene should be taken into consideration.

The catalytic properties of Mo–Ce (sg) complex oxide for selective oxidation of toluene to benzaldehyde without gaseous oxygen in the feed are shown in figure 3. It can be seen that benzaldehyde is the main product and the selectivity is as high as 95.0% every pulse. This indicates that the lattice oxygen ions in Mo–Ce oxides are the main active species for selective oxidation of toluene to benzaldehyde.

The state of lattice oxygen species in the mono-component MoO_3 oxide and Mo–Ce complex oxides was studied by using LRS and TPR. Figure 4 shows the Raman bands of Mo=O species in the complex Mo–Ce oxides. It can be seen that for the complex Mo–Ce (cp) oxide, the vibrational frequency of Mo=O is at 953 cm^{-1}, which is lower than that of Mo=O in MoO_3 (995 cm^{-1}). This red shift of vibrational frequency indicates a weaker Mo=O bonding in the complex Mo–Ce (cp) oxide due to the interaction between molybdenum oxide and cerium oxide. As the lattice oxygen species in the complex Mo–Ce (cp) oxides have higher mobility, their reactivity for selective oxidation of toluene is increased. This can account for the high specific activity of complex Mo–Ce (cp) oxide catalysts for oxidation of toluene to benzaldehyde. Moreover, it can be seen from

Table 1
The catalytic properties of complex Mo–Ce oxide catalysts (Ce/Mo atomic ratio = 1.0) for selective oxidation of toluene to benzaldehyde

Sample	MoO_3	CeO_2	Mo–Ce (cp)	Mo–Ce (sg)
particle size (nm)	> 200	10–20	> 100	20–40
surface area (m^2/g)	5.1	41.0	12.1	19.0
conversion of toluene (mol%)	24.0	54.8	35.5	34.0
benzaldehyde selectivity (%)	6.0	0.0	16.0	37.0
benzaldehyde yield (mol%)	1.4	0.0	5.7	12.6
specific activity ($\mu mol/(s\,m^2)$)	0.4	0.0	0.6	0.9

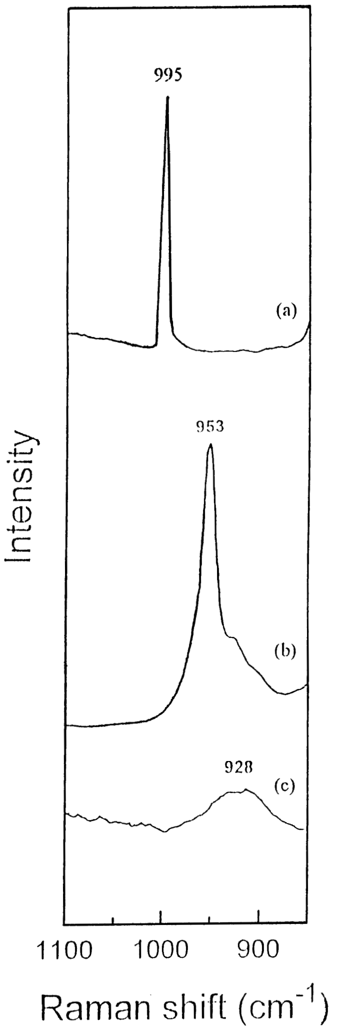

Figure 4. Laser Raman spectra of Mo=O species in mono-component MoO_3 and complex Mo–Ce oxide with a Ce/Mo atomic ratio of 1.0. (a) MoO_3, (b) Mo–Ce (cp), (c) Mo–Ce (sg).

figure 4 that the vibrational frequency of Mo=O species in Mo–Ce (sg) oxide is much lower than that in Mo–Ce (cp) oxide, indicating that Mo=O chemical bonding in the ultrafine oxide particles is even weaker and the lattice oxygen ions have a higher mobility. This leads to the higher reactivity of lattice oxygen ions in the ultrafine oxide particles and, further, the higher benzaldehyde selectivity and specific activity.

The TPR profiles of CeO_2, MoO_3 and Mo–Ce (sg) oxide are shown in figure 5. Two very weak reduction peaks at 510 and 790°C are observed for CeO_2. As reported by Guerrero-Ruiz et al. [16], the hydrogen consumption at lower temperature can be due to the reduction of surface ions, while the reduction peak at higher temperature can be due to the elimination of bulk oxygen anions. For MoO_3, however, three sharp hydrogen consumption peaks at 670, 755 and 990°C are observed, indicating that reduction of molybdenum oxide is easier than that of cerium oxide. By adding ceria to MoO_3, however, the hydrogen consumption peaks shift to lower temperatures: 510, 715 and 860°C. This suggests that due to interaction of Ce with Mo in the complex oxides, the molybdenum oxide is easier to reduce to lower valence. This is consistent with the above LRS results.

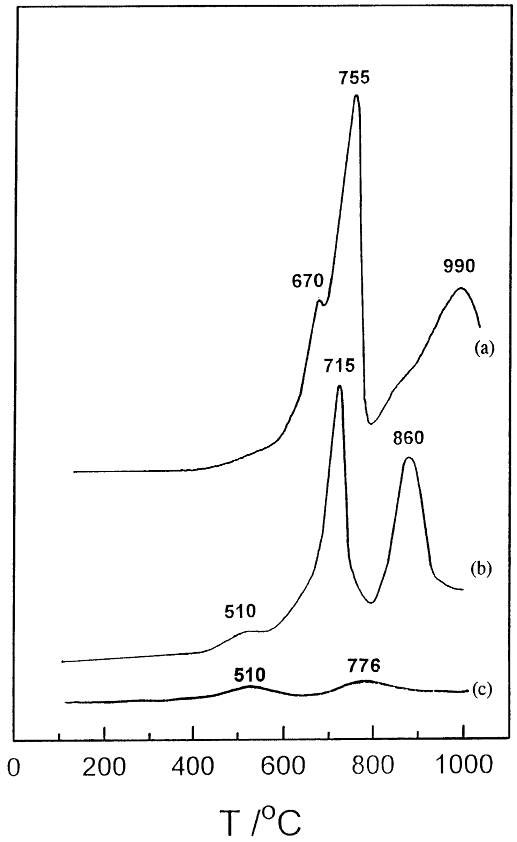

Figure 5. TPR profiles of the mono-component CeO_2, MoO_3 and Mo–Ce (sg) oxide catalyst with a Ce/Mo atomic ratio of 1.0. (a) MoO_3, (b) Mo–Ce (sg), (c) CeO_2.

Based on the above results, it is concluded that the higher reactivity of lattice oxygen in the matrix of ultrafine complex Mo–Ce oxides can account for the reason that ultrafine complex oxide particles exhibit unique catalytic properties for selective oxidation of toluene to benzaldehyde. Our results have clearly confirmed that the reactivity of lattice oxygen ions can be improved by decreasing the oxide particle size to nanoscale.

4. Conclusion

For selective oxidation of toluene to benzaldehyde the ultrafine Mo–Ce oxide particles prepared by the sol–gel method exhibit higher catalytic activity than the larger oxide particles prepared by conventional coprecipitation method. The unique catalytic properties of ultrafine Mo–Ce oxide particles may be correlated not only to the interaction between molybdenum and cerium oxide, but also to the higher reactivity of lattice oxygen species in the ultrafine oxide matrix.

Acknowledgement

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